PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Serial No.:	10/681,422
Filed:	October 8, 2003
Art Unit:	1712
Examiner:	Michael J. Feely
Applicant:	William J. van Ooij et al.
Title:	Silane Compositions and Methods for Bonding Rubbers to Metals
Atty Ref.:	UOC-171
Conf. No.:	7421

DECLARATION OF WILLIAM J. VAN OOIJ
PURSUANT TO 37 C.F.R. § 1.132

I, William J. van Ooij, declare as follows:

1. I am a joint inventor of the above captioned matter and make this declaration in support thereof. A copy of my curriculum vitae is attached hereto.

2. I am not being separately compensated for my work related to this declaration.

3. I earned a Master of Science degree, with highest honors, in Chemical Engineering and a Doctor of Philosophy, with highest honors, in Physical Chemistry, both from Delft University of Technology in The Netherlands.

4. I have been actively involved for the past twenty years in silane chemistry, in particular, silane coatings for bonding metal to rubber and for corrosion control of metal surfaces. I began my career with Ames Laboratory in 1971 as a Postdoctoral Associate and became actively involved in silane chemistry technologies at Colorado School of Mines in 1986. Since that time, I have had numerous roles and responsibilities in teaching and research and development, culminating in my present role as Professor at the University of Cincinnati in

the Department of Chemical and Materials Engineering where I have continued to teach and research and develop silane chemistry technologies.

5. During my career, I have received numerous awards and recognitions throughout the world for my research and achievements, particularly in the area of silane chemistry. I also have chaired various professional associations and committees, including the First International Conference on Adhesion Science and Technology held in The Netherlands in 1995.

6. I believe that I am qualified to address issues regarding silane chemistry technologies, including methods of bonding rubber to metal using silane coatings, as well as the distinct differences between the above captioned case and the silane technology disclosed in Pines U.S. Patent No. 3,088,847 ("Pines"), Van Ooij WO 00/63462 ("the '462 application"), Van Ooij U.S. Patent No. 6,416,869 ("the '869 patent"), and Van Ooij U.S. Patent No. 6,756,079 ("the '079 patent") (collectively, "the Van Ooij references"), currently cited by the Examiner.

7. I am familiar with the prosecution of the above-referenced matter. In particular, I have read the above captioned patent application, the pending claims (as presented in the July 3, 2007 Response), and the September 14th Official Action ("Official Action"), including the Pines reference.

8. Having considered these materials, I understand that the Examiner continues to reject claims 26-35, 41-43, 97, and 98 as being obvious over the combination of the '462 application, "the '869 patent, or the '079 patent in view of Pines. And, further continues to reject claims 36-40, 46-55, 99, and 100 as being obvious over the '462 application, the '869 patent, or the '079 patent in view of Pines and further in view of Shimakura U.S. Patent No. 6,475,300, ("Shimakura"). In particular, Examiner asserts that it would have been obvious to one of ordinary skill in the art to use a coating thickness of from about 0.1 μm to about 1 μm or from about 0.2 μm to about 0.6 μm, as allegedly taught by Pines, in the method of the Van Ooij

references, because Pines allegedly discloses a similar method of using an aminoalkyl-alkoxy silanes to bond rubber to metal, wherein film thicknesses ranging from 0.01 to 0.10 mil (0.254 µm – 2.54 µm) are preferred. *See* Official Action, Page 4, for example. I respectfully disagree for the reasons that follow.

9. In comparison to the Van Ooij references, as well as the presently claimed invention, Pines does not at all disclose a similar method for bonding rubbers to metals. In particular, Pines specifically discloses silicone rubber (a saturated polymer) and neoprene, a diene rubber, for example, which are peroxide-cured rubbers, not sulfur-cured rubbers. Our rubber is sulfur cured. In addition, the silanes taught by Pines are an amino silane (and copolymers of the amino silane) <u>and</u> a vinyl silane. These silanes have been found by me to be inactive to rubbers of the diene type when cured by sulfur (and sulfenamide accelerators). To that end, the silane system of the Van Ooij references and that of the present invention consist of two specific silanes, preferably in a certain ratio. One of them must contain sulfur, the other contains a secondary amino group. This silane mixture of bis-sulfur and bis-amino silane is quite different from that of Pines and the only silane process, thus far, that we have found to bond to sulfur-cured rubbers. In fact, we have tested dozens of other silanes before we discovered the bis-sulfur/bis-amino mixture, but the results were all negative, i.e., no or very poor bond strength was obtained. So, this mixture and coating method are unique and quite different from Pines.

10. In addition, the silanes of Pines are so-called mono-silanes, i.e., each molecule contains only one trialkoxysilyl group. In contrast, the silanes that are used in the Van Ooij references and the present application are bis-silanes, also called di-podal silanes, which contain two trialkoxysilyl groups, one on each end of the molecule. I have tested the mono versions of the two silanes, viz., γ-aminopropyl triethoxy silane and mercapto trimethoxy silane, but the results were negative. No adhesion to speak of was obtained. Thus, there is not only the

need for a specific mixture of silanes, i.e. amino and sulfur silanes, for bonding metals to sulfur-vulcanized rubber, there is also the requirement that the silanes be of the bis-silane type.

11. Furthermore, in terms of mechanisms of bonding, there are also substantial and fundamental differences with Pines and that of the Van Ooij references and the present invention. The bond formation in Pines relies on the oxidation of the silane film by the peroxide in the rubber. The oxidation leads to the formation of covalent C-C bonds between the surface of the silane film, a primer, and the rubber coating. This explains why the thickness of the silane film in Pines is not at all critical, as only the surface of the silane film contributes to the bond strength. It further explains why Pines uses a vinyl silane as a second silane, rather than a sulfur silane, for example. The vinyl group (-C=C-) is very easily oxidized by peroxides. The choice of the γ-aminopropyltriethoxy silanes by Pines is also understandable, as the R group in –N-R-Si≡ is also easily oxidized by peroxides. The primary amine group ($-NH_2$) plays no direct role in the bond formation but it makes the –R group ($-CH_2CH_2CH_2-$) more sensitive to oxidation by peroxides.

12. In the rubber-silane-metal system of the present application, the sulfur silane is essential, as during the cure it will decompose into Si-R-S• radicals which are reactive towards the –C=C-C- groups in the rubber. The monosilanes containing sulfur do not form such radicals so therefore they do not bond to rubber. The bis-amino silane in our mixture is required, as the secondary amino groups –NH– have a catalytic activity for crosslinking ethylsilyl groups in the absence of water, i.e., without hydrolysis.

$$\equiv Si\text{-}OC_2H_5 + H_5C_2O\text{-}Si\equiv \xrightarrow{-NH-} \equiv Si\text{-}O\text{-}Si\equiv + H_5C_2OC_2H_5$$

This explains why we need the bis-amino silane, as the monoamino silanes, e.g., the type used in the Pines patent, has a primary amino group which has considerable lower catalytic activity.

13. In view of the teachings in Pines, it is abundantly clear to one skilled in the art that Pines does not at all disclose a similar method for bonding rubbers to metals like that discussed in the Van Ooij references or the present invention. In other words, there is nothing in Pines that would lead one skilled in the art to combine it with any of the Van Ooij references. Indeed, the clearly different silane composition of Pines, and its non-critical coating thickness, provide no rationale basis to form a coating thickness of from about 0.1 μm to about 1 μm using the bis amino/bis sulfur silanes of the Van Ooij references.

14. From the discussion in the foregoing it may be concluded that the use of a specific coating thickness, which coating includes two bis-silanes, i.e., bis-sulfur and bis-amino, for bonding metals to sulfur-cured rubber, as required by claims 26 and 46, is by no means obvious and cannot be predicted from the combination of the Pines patent and the Van Ooij references, not even by someone skilled in the art. Simply stated, the Pines coating thickness is not at all applicable to Applicants' method.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-referenced patent application as originally filed and/or any patents to be issued and/or granted thereon.

William J. van Ooij

Feb. 14, 2008
Date

WIM J. VAN OOIJ

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Ph.D.* (Physical Chemistry)	1971	Delft University of Technology (The Netherlands)
M.S.* (Chemical Engineering)	1964	Delft University of Technology (The Netherlands)

** with highest honors*

Professional and Society Affiliations

·American Chemical Society
·The Adhesion Society
·NACE
·Materials Research Society
·Royal Dutch Chemical Society
·China Ordnance Research Society
·American Society for Materials

Fields of Special Interest

·Corrosion Control of Metals by Organic Coatings
·Chemistry of Silanes at Metal Surfaces
·Surface Analysis of Materials
·Secondary Ion Mass Spectrometry
·Electrochemical Impedance Spectroscopy
·Plasma-Polymerized Coatings

Honors and Awards

- UC Special Achievement Award 2006 (for Submitting 100 Invention Disclosures)
- UC Emerging Entrepreneur Award 2005
- Program Chairman, ASM Surface Engineering Congress, Orlando, FL, August 2-4, 2004
- R&D 100 Award 2000 for Galv-Gard® Technology
- UC College of Engineering Research Award (2000)
- Royal Society of Chemistry's Industrial Innovation Team Award 1999 (UK)
- R&D 100 Award 1999 for OXSILAN® Technology
- UC Faculty Achievement Award (University of Cincinnati; 1999)
- BFGoodrich Collegiate Inventors Program Award (1997)
- UC Faculty Achievement Award (University of Cincinnati; 1994)
- Plueddemann Award for Excellence in Research on Interfaces (1994)
- Armco Technical Achievement Award (1992)
- Chairman of the Organizing Committee of the First International Conference on Adhesion Science and Technology, October 16-20, 1995, Amsterdam, The Netherlands
- Listed in MEN OF ACHIEVEMENT, International Biographical Centre, Cambridge, England, Sixteenth Edition (1993)
- Listed in WHO'S WHO IN THE MIDWEST (1991-to date)
- Listed in WHO'S WHO IN SCIENCE AND ENGINEERING (1997)
- Editorial Board Plasmas and Polymers (1994-to date)
- Editorial Board Progress in Organic Coatings (1987-to date)
- Editor-in-Chief Journal of Adhesion Science and Technology (1987-to date)
- Editorial Board Surface and Interface Analysis (1985-1987)
- Unilever Gold Medal for Outstanding Students of Chemistry in The Netherlands (1963)

Experience

9/93 -	University of Cincinnati, Professor, Department of Materials Science and Engineering
5/89 - 9/93	Armco Research & Technology, Middletown, Ohio, Senior Staff Scientist
8/86 - 5/89	Colorado School of Mines, Golden, CO, Professor, Department of Chemistry
6/85 - 7/86	Virginia Tech, Blacksburg, VA, Visiting Professor, Dept. of Materials Engineering
4/73 - 6/85	Akzo Research Laboratories, Arnhem, The Netherlands, Senior Research Chemist
3/71 - 4/73	Ames Laboratory at Iowa State University, Postdoctoral Associate
2/64 - 3/71	Delft University of Technology, Interuniversity Reactor Institute, Sr. Research Associate

Publications

Over 350 technical and scientific publications and >50 patents with Akzo Corporate Research, 3M, Pirelli SpA (Italy), Armco Research & Technology, Brent America, Chemetall GmbH, Procter & Gamble, SENCO, University of Cincinnati, Chemat Technologies, and Vernay Laboratories. Complete list available upon request.